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- (21) Application No. 2738/78 (22) Filed 24 Jan. 1978 (19)  
(31) Convention Application No.'s 52/007305 (32) Filed 27 Jan. 1977  
52/007305 1 Jul. 1977  
52/128776 28 Oct. 1977  
52/128776 25 Jan. 1978 in  
(33) Japan (JP)  
(44) Complete Specification Published 19 Sep. 1979  
(51) INT. CL.<sup>2</sup> F16L 11/12  
(52) Index at Acceptance  
F2P 1A13 1A27 1B7  
B5A 1R314C1B 1R429X 20T10 20T17 D31



(54) PROCESS FOR PRODUCING MICROPOROUS TUBE  
OF A VINYLIDENE FLUORIDE POLYMER

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA a Japanese Company of No. 1-8 Horidome-cho, Nihonbashi, Chuou-Ku, Tokyo, Japan do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:-

This invention relates to a process for producing a microporous tube of a vinylidene fluoride polymer. More specifically, it relates to a process for producing a microporous tube of a vinylidene fluoride polymer which has a uniform pore size and can be used for microfilters or ultrafilter membranes.

Separation using membranes has been employed in various fields as one technique of separating and recovering a substance from a solution, and many kinds of membranes with different pore sizes, materials and methods of production have been used depending on the particular applications involved. Of these, separation membranes having a pore diameter below 0.1 micron are called ultrafilter membranes, and are used for ultrafiltration, that is separation technique whereby in a solution under pressure, high-molecular-weight material or colloidal substances are retained by the membrane and water and low-molecular-weight materials present in a solvent are allowed to pass through the membrane. Since the ultrafiltration process does not involve heating or the addition of a flocculating agent, this process has advantages over other separation techniques, such as distillation, sedimentation under reduced pressure, pressure floatation, ultracentrifugal separation, flocculation sedimentation or electrolytic floatation, in that separation, concentration, recovery and purification can be performed without degenerating the substances present. Ultrafiltration is, therefore, very suitable for operations such as the concentration and purification of influenza vaccine, the concentration and purification of proteins containing amino acids or salts, and the concentration of dilute emulsion latices. This process can also be utilized for separating materials from various waste waters and liquors to prevent secondary pollution or to conserve resources.

Materials for ultrafilter membranes also determine the properties of the membranes. The dynamic strength, acid resistance, alkali resistance, oil resistance and water resistance of the membranes are important factors which determine the range of application and the lifetime of the membranes. These factors depend almost unequivocally upon the materials used. Microporous tubes are a new type of ultrafilter membranes, and have the advantage that filtration pressures can be made higher than in flat membranes, and the membrane area per unit volume of filter can be increased.

A vinylidene fluoride polymer is a polymeric material which contains a fluorine atom, which has high dynamic strength, superior chemical properties (i.e., high resistances to alkalis, oils and water) and which has good heat processability, and is very desirable as a material for membranes.

A method for utilizing a vinylidene fluoride polymer as a porous structure has already been suggested which comprises heating and compressing a fine powder of vinylidene fluoride polymer to sinter the particles to one another. For example, British Patent 1,282,390 discloses a method for the production of an ink-feeding and writing core for writing instruments using a sintered porous film of polyvinylidene fluoride. This prior art method, however, is not suitable for obtaining uniform pore diameters for a number of reasons. For example, because the fine powder is compressed at a temperature above its

softening temperature, the powder tends to deform and a uniform particle diameter is difficult to obtain. Furthermore, the powder tends to flow on melting and sometimes pores are not formed. A membrane with a smaller pore diameter would be obtained if the particle diameters of the fine powder were smaller. However, for the reason given above, a porous structure is difficult to obtain from a fine powder with a small particle diameter, and in practice, this known method can only be applied to fine powders having a particle diameter of about 50 to about 60 microns, and cannot be used with the particle diameters required to produce microporous structures, i.e. 0.1 micron.

An object of this invention is therefore to provide a method of producing a microporous tube of a vinylidene fluoride polymer which can be used as an ultrafilter membrane. According to this invention, there is provided a process for producing a microporous tube of a vinylidene fluoride polymer comprising the steps of:-

(a) extruding a molten vinylidene fluoride polymer into a tubular form and crystallizing the vinylidene fluoride polymer while flow-orienting the molten vinylidene fluoride polymer to form a starting tube which has a birefringence of  $15 \times 10^{-3}$  to  $30 \times 10^{-3}$  and where the crystals of the starting tube of the vinylidene fluoride polymer show a sharp single endothermic peak when melted;

(b) heat-treating the starting tube in the substantial absence of affirmatively applied tension at a temperature of 80 to 170°C for at least 3 seconds;

(c) stretching the tube by a stretch ratio of 20 to 200% of the original length of the tube at a temperature of 10 to 100°C; and

(d) heat-treating the stretched tube under tension at a temperature of 80 to 160°C for at least 3 seconds.

The method described in the preceding paragraph produces a novel microporous tube of a vinylidene fluoride polymer having the following characteristics:-

(1) the apparent density of the microporous tube is not more than about 90% of the inherent density of the vinylidene fluoride polymer, i.e., the inherent density of the microporous tube is about 90% or less of the inherent density of the vinylidene fluoride polymer used, and

(2) most of the pores in the microporous tube have a pore diameter distributed between 0.01 and 0.1 micron, with the pores extending from the inside of the tube to the outside of the tube.

The tube which can be used in this invention is a hollow substance and no limitation exists on the diameter thereof. In general however, a suitable outside diameter is preferably 0.02 to 50mm, more preferably 0.05 to 10mm. For example, a hollow fiber-like material is included in the definition of a tube according to this invention. However, it is generally difficult to produce a hollow fiber of a vinylidene fluoride polymer having a diameter of less than about 20 microns and even if produced, it is extremely difficult to obtain a uniform fiber-like tube. Therefore, a preferred outside diameter of the tube is about 20 microns or more. Further, where the tube is used as a filtration membrane, in order to make the effective area of the filtration as large as possible, it is advantageous for the outside diameter to be as small as possible. From this standpoint, an especially preferred outside diameter of the tube is 50mm or less.

The term "vinylidene fluoride polymer", as used in the present application, denotes not only a homopolymer of vinylidene fluoride, but also copolymers containing at least 90 mole% of vinylidene fluoride units which have characteristics equivalent to those of the vinylidene fluoride homopolymer. Examples of comonomers copolymerizable with vinylidene fluoride are tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene, vinyl fluoride, perfluoroisobutylene and perfluorovinyl ether.

A suitable inherent viscosity ( $\eta_{inh}$ ) for the vinylidene fluoride polymer used as a starting material in the method of this invention ranges from 0.4 to 1.8, preferably 0.6 to 1.5, (measured as a solution of vinylidene fluoride polymer having a concentration of 0.4 g/ml using dimethylacetamide as the solvent at 30°C), where the inherent viscosity ( $\eta_{inh}$ ) is expressed by the relationship

$$\eta_{inh} = \frac{1}{C} \ln \frac{\eta}{\eta_0}$$

wherein  $\eta$ : viscosity of the solution of the vinylidene fluoride polymer in dimethylacetamide at a concentration of 0.4 g/ml at 30°C;

$\eta_0$ : viscosity of dimethylacetamide at 30°C;

C: concentration (=0.4 g/ml).

The production of the microporous tube starts from a starting tube which has a specified birefringence which represents the degree of molecular orientation. The starting tube should have a birefringence, measured by the sodium D-line, of  $15 \times 10^{-3}$  to  $30 \times 10^{-3}$ , and the crystals of the starting tube should show a sharp single endothermic peak when heated

at a rate of 8°C/min. in an atmosphere of nitrogen gas using a differential scanning calorimeter to melt the crystals.

5 The tube which exhibits a birefringence is obtained by crystallizing a vinylidene fluoride polymer in the molten state while flow-orienting the vinylidene fluoride polymer. The starting tube in accordance with this invention should have a birefringence of  $15 \times 10^{-3}$  to  $30 \times 10^{-3}$ , preferably  $20 \times 10^{-3}$  to  $25 \times 10^{-3}$ . Tubes having a birefringence of less than  $15 \times 10^{-3}$  or more than  $30 \times 10^{-3}$  show a double endothermic peak when the crystals of the starting tube are melted. Thus, these tubes are unsuitable for use as starting tubes in the present invention.

10 The starting tubes used in this invention can be obtained by heat processing a vinylidene fluoride polymer using a conventional extruder equipped with a die for tube production. Suitable extrusion temperatures or die temperatures which can be used range from about 180 to about 300°C, preferably from 190 to 260°C. At the time of extrusion, care should be taken to avoid the occurrence of melt fracture in the tubular molten vinylidene fluoride polymer which flows through the die. This is a concern observed in general in the melt processing of conventional plastics, and it is not a special condition for producing the starting tube used in this invention. In order to maintain the tubular molten vinylidene fluoride polymer which flows through the die in a tubular state until the polymer is cooled, crystallized (e.g., at about 160°C or less) and solidified, it is possible to introduce into the tube through the die orifice either air or a gas (e.g., nitrogen gas or helium gas) or liquid (e.g., water or an oil) inert to the vinylidene fluoride polymer. The solidified tube can be taken up through guide rolls using conventional methods.

15 The birefringence of the starting tube depends upon the drawdown ratio ( $A_1/A_2$ ) which is the ratio of the sectional area ( $A_1$ ) of the flow inlet of the die to the sectional area ( $A_2$ ) of the tube, and upon the rate of cooling the melt, and increases with increasing draw-down ratio and increasing rate of cooling. Thus, the birefringence of the tube varies according to the temperature of the molten vinylidene fluoride polymer, the rate of the take up of the molten polymer, and the method of cooling as well as the prescribed draw-down ratio. It is therefore impossible to define unequivocally the conditions for obtaining starting tubes having the required birefringence which represents the degree of molecular orientation. However, when the temperature of the flowing molten vinylidene fluoride polymer is about 200°C to 240°C and the tube is cooled with air, the preferred draw-down ratio is about 30 to 110.

20 Since the resulting starting tube has a residual internal strain, the tube is heat-treated in the substantial absence of any affirmatively applied tension at a temperature of 80 to 170°C for at least 3 seconds in order to remove the residual tension. For example, the heat-treatment can be performed for up to 24 hours, although normally the maximum heat treatment time is 1 hr.

25 The heat-treated tube is then stretched at a stretch ratio of 20 to 200% and a temperature of 10 to 100°C, whereby numerous open pores with a pore diameter of 0.01 to 0.2 micron are formed in the wall of the starting tube. The stretch ratio is defined by the following equation.

30

$$\text{Stretch Ratio (\%)} = \frac{(\text{Length after stretching}) - (\text{Length before Stretching})}{(\text{Length before Stretching})} \times 100$$

45

If the stretching stress is released, the pores of the tube shrink as the entire tube shrinks. Thus, the tube must be stabilized by immediately subjecting the tube to the subsequent heat-treatment without releasing the stress due to stretching. Specifically, the microporous tube in accordance with this invention can be obtained by maintaining the tube having pores formed therein at a temperature of 80 to 160°C for at least 3 seconds under tension of 200 to 5000 g/mm<sup>2</sup>.

50 Since pores are formed due to the stretching operation, the pore volume naturally increases with higher stretch ratios. Hence, the apparent density of the resulting microporous tube decreases, and becomes not more than 90% of the inherent density of the vinylidene fluoride polymer.

55 The pore volume and pore diameter of the microporous tube can be determined using mercury porosimetry [the method described in Richard G. Quynn, *Test. Res. J.*, 33, 21 (1963)] and values given herein relative thereto are using this method.

60 The foregoing description has been directed to the use of vinylidene fluoride polymer alone. It will be obvious to those skilled in the art that within the ranges which do not greatly affect the crystallinity of the vinylidene fluoride polymer, various pigments, e.g., TiO<sub>2</sub> or Cr<sub>2</sub>O<sub>3</sub>, nucleating agents such as potassium chloride, plasticizers such as low-molecular-weight polyesters or other polymers compatible with the vinylidene fluoride polymer, such as poly(methylmethacrylate) can be added to the vinylidene fluoride polymer as desired. A suitable amount of these conventional addenda is preferably about 65

0.1 to about 10% by weight based on the weight of the vinylidene fluoride polymer.

In the accompanying drawings,

5 *Figure 1* is a graphical representation showing the melting behavior of crystals of a vinylidene fluoride polymer which is determined using a differential scanning calorimeter, No. 4 referring to a starting tube used in a method in accordance with one example of this invention, and Nos. 1 and 6, to tubes having different birefringence; and 5

10 *Figure 2* is a graphical representation showing the pore diameter distribution, determined using the mercury porosimeter method, of a microporous tube of a vinylidene fluoride polymer produced in accordance with said one example of this invention which was obtained by stretching at stretch ratio of 100%. 10

Referring to the drawings, the following Examples are given to illustrate the present invention more specifically. Unless otherwise indicated herein, all parts, percents, ratios and the like are by weight.

15

#### *Example 1*

15

20 A vinylidene fluoride homopolymer (Kureha KF Polymer # 100, tradename for a product of Kureha Kagaku Kogyo Kabushiki Kaisha; inherent viscosity  $\eta_{inh} = 1.01$ ) was extruded through a die (outside diameter: 10 mm; inside diameter: 9 mm) directed downwardly using an extruder with a diameter of 20 mm (the ratio of barrel length L to the diameter D, L : D was 26 : 1). The temperature of the die was set at 220°C. The tube which flowed from the die was forcedly cooled with air immediately below the die, and the tube taken up using a variable speed take-up device through guide rolls positioned at a distance of 85 cm from the tip of the die. 20

25 By varying the take-up rate, six tubes having different draw-down ratios were prepared. The outside and inside diameters, the birefringences and the peak temperatures of the endotherm on melting of the crystals determined using a differential scanning calorimeter of these tubes are shown in Table 1 below. 25

Table 1

Sample No.	Draw-down Ratio	Outside Diameter of Tube (mm)	Inside Diameter of Tube (mm)	Birefringence of Tube ( $\times 10^{-3}$ )	Peak Endothermic Temperatures of Melting Crystals (°C)	
1	14	2.65	2.4	12	170	175
2	35	1.7	1.5	15	Very slight endotherm at 170	174
3	52	1.4	1.25	18	-	174
4	70	1.2	1.1	22	-	174
5	104	1.0	0.9	25	-	175
6	139	0.35	0.75	32	-	Very slight endotherm at 194
						194

It can be seen that Samples Nos. 2, 3, 4 and 5 showed a single endothermic peak at the time of the melting of the crystals, and Samples Nos. 1 and 6 showed a double peak. The melting behaviour curves of Samples Nos. 1, 4 and 6 determined using a differential scanning calorimeter are shown in Figure 1.

#### Example 2

Each of the tubes obtained in Example 1 was heat-treated at 135°C for 10 minutes in the absence of any tension. The heat-treated tube was then stretched at 23°C at a stretch ratio of 100%, and, without releasing the stretching stress, the tube was heat-treated at 135°C for 10 minutes. The apparent densities and pore volumes of the stretched tubes are shown in Table 2 below.

Table 2

Sample No.	Apparent Density (g/cm <sup>3</sup> )	Pore Volume (cm <sup>3</sup> /g)
1-100	1.66	0.037
2-100	1.59	0.064
3-100	1.54	0.084
4-100	1.53	0.089
5-100	1.58	0.068
6-100	- (1)	- (1)

(1) Tube broke when the stretch ratio reached 80%, and a sample could not be prepared.

The results in Table 2 above show that of Samples Nos. 2, 3, 4 and 5 which has a birefringence of  $15 \times 10^{-3}$  to  $25 \times 10^{-3}$  and showed a single endothermic peak on melting of the crystals, those samples having a birefringence of  $18 \times 10^{-3}$  to  $22 \times 10^{-3}$  gave stretched tubes having an especially low apparent density and an especially large pore volume when stretched.

#### Example 3

Three tubes, similar to Sample No. 4 in Example 1, were prepared and heat-treated at 135°C for 10 minutes in the absence of any tension. The tubes were each stretched at 23°C at varying stretch ratios, and immediately heat-treated at 150°C for 10 minutes, followed by cooling to 25°C. The stretch ratios and the apparent densities and pore volumes of the resulting tubes are shown in Table 3 below.

Table 3

Sample No.	Stretch Ratio (%)	Apparent Density (g/cm <sup>3</sup> )	Pore Volume (cm <sup>3</sup> /g)
4-030	30	1.60	0.060
4-050	50	1.57	0.072
4-100	100	1.53	0.089
4-180	180	1.51	0.099

The pore diameters of the tubes were measured by mercury porosimetry, and it was found that most of the pore sizes were distributed between 0.01 and 0.1 micron. The pore size distribution curve of Sample No. 4-100 is shown in Figure 2.

#### Example 4

The strength of the microporous tube (Sample No. 4-100 of Example 3) was measured using a tensile tester (Model UTM-III, a product of Toyo Baldwin Company) at a pulling rate of 100 mm/min. The results obtained are shown in Table 4.

Table 4

	Direction of Measurement	Tensile Strength (kg/mm <sup>2</sup> )	
5	Parallel to axis of Tube	13.2	5
10	Perpendicular to axis of Tube	2.9	10

Since this tube had an outside diameter of 0.9 mm and an inside diameter of 0.82 mm, its compressive strength was calculated as 2.9 kg/cm<sup>2</sup>.

15	<i>Example 5</i>		15
20	The tip of each of the tubes designated as Sample No. 4 (unstretched tube) of Example 1 and Sample No. 4-100 (stretched microporous tube) of Example 3 was sealed by welding, and the other end was connected to a feed opening for nitrogen gas under a pressure of 1 kg/cm <sup>2</sup> -G. The entire tube was immersed in water, and nitrogen gas bubbles released from the tube were collected in a glass bottle. Under the same conditions, more than 1000 times as much nitrogen gas was corrected from the tube of Sample No. 4-100 as from the tube of Sample No. 4.		20
25	<i>Example 6</i>		25
	The microporous tube of Sample No. 4-100 of Example 3 was immersed in each of several typical chemical materials at 50°C for 1 month, and then the strength of the tube was measured. The results obtained are shown in Table 5 below.		

Table 5

				Strength (kg/mm <sup>2</sup> )		
35	Chemical Material	Temperature (°C)	Immersion Time	Parallel to axis of Tube	Perpendicular to axis of Tube	35
40	5% NaOH	50	1 month	13.5	3.0	40
	20% HCl	"	"	13.3	3.0	
	n-Hexane	"	"	13.0	3.0	
45	Benzene	"	"	12.5	2.7	45
50	Carbon Tetrachloride	"	"	12.5	2.8	50
	Water	"	"	13.3	3.0	

It was found that the tube was scarcely deteriorated by the chemical materials shown in Table 5 above.

55	The tube was exposed to a Sunshine Weather-Ometer WE-SUN-TC (a product of Toyo Rika Kogyo Kabushiki Kaisha) at 63°C for 1,000 hours, but hardly any change in strength occurred. After exposure, the strength of the tube was 13.5 kg/mm <sup>2</sup> in a direction parallel to the axis of the tube, and 3.0 kg/mm <sup>2</sup> in a direction perpendicular to the axis of the tube. This means that the tube was very stable to ultraviolet irradiation.	55
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60	<i>Example 7</i>		60
65	A copolymer of vinylidene fluoride and chlorotrifluoroethylene having a vinylidene fluoride content of 97 mole%, a density of 1.78 g/cm <sup>3</sup> and an inherent viscosity ( $\eta_{inh}$ ) of 0.99 was extruded from the same die using the same extruder as in Example 1. The temperature of the die was set at 200°C. A starting tube having a draw-down ratio of 80, an outside diameter of 1.1 mm and an inside diameter of 1.0 mm was obtained. This starting tube had a		65

birefringence of  $22 \times 10^{-3}$  and exhibited a single endothermic peak at 165°C when the crystals were melted using a differential scanning calorimeter.

The starting tube was heat-treated at 120°C for 30 minutes in the absence of any tension, stretched at 23°C by 100%, and immediately heat-treated at 120°C for 30 minutes, followed by cooling to 25°C.

The stretched tube had an apparent density of 1.54 g/cm<sup>3</sup> and a pore volume of 0.087 cm<sup>3</sup>/g, and an average pore diameter of 0.15 micron as determined using mercury porosimetry.

#### Example 8

A tube having an outer diameter of 0.1 mm and an inner diameter of 0.05 mm was prepared using the same polymer as described in Example 1 and in the same manner as described in Example 1 except using a draw-down ratio of 100.

The starting tube had a birefringence of  $23 \times 10^{-3}$  and exhibited a single endothermic peak at 174°C when the crystals were melted.

The starting tube was heat-treated and stretched under the same conditions as described in Example 2.

The stretched porous tube had an average pore diameter of 0.05 micron and a pore volume of 0.090 cm<sup>3</sup>/g as determined using mercury porosimetry.

#### Example 9

The same vinylidene fluoride homopolymer as described in Example 1 was extruded through a die (outside diameter: 9.5 mm; inside diameter: 7.6 mm) directed downwardly using the same extruder as was used in Example 1. The temperature of the die was set at 205°C. The tube which flowed from the die was taken up (draw-down ratio: 73) and cooled under the same conditions as described in Example 1 to obtain a starting tube (outside diameter: 1.0 mm; inside diameter: 0.8 mm). The starting tube had a birefringence of  $21 \times 10^{-3}$ .

The starting tube was heat-treated at each of the temperatures as shown in Table 6 below for 3 hours in the absence of any tension. Each of the heat-treated tubes was then stretched at 20°C at a stretch ratio of 120%, heat-treated at 135°C for 10 minutes and immediately cooled to room temperature (23°C).

The apparent densities and pore volumes of the resulting microporous tubes obtained are shown in Table 6 below.

Table 6

Heat-Treatment Temperature of Starting Tube (°C)	Apparent Density (g/cm <sup>3</sup> )	Pore Volume (cm <sup>3</sup> /g)
120	1.44	0.129
145	1.44	0.129
155	1.42	0.139
165	1.38	0.160
170	1.37	0.165

The pore diameters of the tubes were measured by mercury porosimetry, and it was found that the pore sizes were distributed between 0.01 and 0.1 micron. The average pore size was 0.05 to 0.06 micron.

#### Example 10

A copolymer of vinylidene fluoride and vinyl fluoride having a vinylidene fluoride content of 93 mole% and a vinyl fluoride content of 7 mole%, a density of 1.75 g/cm<sup>3</sup> and an inherent viscosity ( $\eta_{inh}$ ) of 1.00 was extruded from the same die using the same extruder as in Example 1. The temperature of the die was set at 200°C. A starting tube having a draw-down ratio of 70, an outside diameter of 1.0 mm and an inside diameter of 0.9 mm was obtained. This starting tube had a birefringence of  $21 \times 10^{-3}$  and exhibited a single endothermic peak at 169°C when the crystals thereof were melted using a differential



scanning calorimeter.

The starting tube was heat-treated at 135°C for 30 minutes in the absence of any tension, stretched at 23°C at a stretch ratio of 100% and immediately heat-treated at 120°C for 10 minutes, followed by cooling to room temperature (23°C).

- 5 The microporous tube obtained had an apparent density of 1.55 g/cm<sup>3</sup>, and a pore volume of 0.075 cm<sup>3</sup>/g and an average pore size of 0.045 micron as determined using mercury porosimetry. 5

WHAT WE CLAIM IS:

1. A process for producing a microporous tube of a vinylidene fluoride polymer comprising the steps 10

(a) extruding a molten vinylidene fluoride polymer into a tubular form and crystallizing the molten vinylidene fluoride while flow-orienting the vinylidene fluoride polymer to form a starting tube which has a birefringence of  $15 \times 10^{-3}$  to  $30 \times 10^{-3}$  and where the crystals of the starting tube of the vinylidene fluoride polymer show a sharp single endothermic peak 15 when melted;

(b) heat-treating the starting tube in the substantial absence of affirmatively applied tension at a temperature of 80 to 170°C for at least 3 seconds;

(c) stretching the tube by a stretch ratio of 20 to 200% of the original length of the tube at a temperature of 10 to 100°C; and

- 20 (d) heat-treating the stretched tube under tension at a temperature of 80 to 160°C for at least 3 seconds. 20

2. A process as claimed in claim 1, wherein the starting tube has a birefringence of  $20 \times 10^{-3}$  to  $25 \times 10^{-3}$ .

3. A process as claimed in claim 1 or claim 2 wherein the vinylidene fluoride polymer is a homopolymer of vinylidene fluoride or a copolymer of at least 90 mole % of vinylidene fluoride with a monomer copolymerizable with vinylidene fluoride. 25

4. A process as claimed in any one of the preceding claims, wherein most of the pores of the microporous tube have a diameter in the range of 0.01 to 0.2 microns.

5. A process as claimed in claim 4, wherein most of the pores of the microporous tube have a diameter in the range of 0.01 to 0.1 micron. 30

6. A process as claimed in any one of the preceding claims, wherein the microporous tube has an apparent density of not more than 90% of the inherent density of the vinylidene fluoride polymer.

7. A process as claimed in claim 1 for producing a microporous tube of a vinylidene fluoride polymer substantially as hereinbefore described with reference to the Examples. 35

8. A microporous tube of a vinylidene fluoride polymer produced by the process of Claim 1.

9. A microporous tube of a vinylidene fluoride polymer wherein the tube has an apparent density of not more than 90% of the inherent density of the vinylidene fluoride polymer, and the majority of the pores in the tube have a diameter in the range of 0.01 to 0.2 micron. 40

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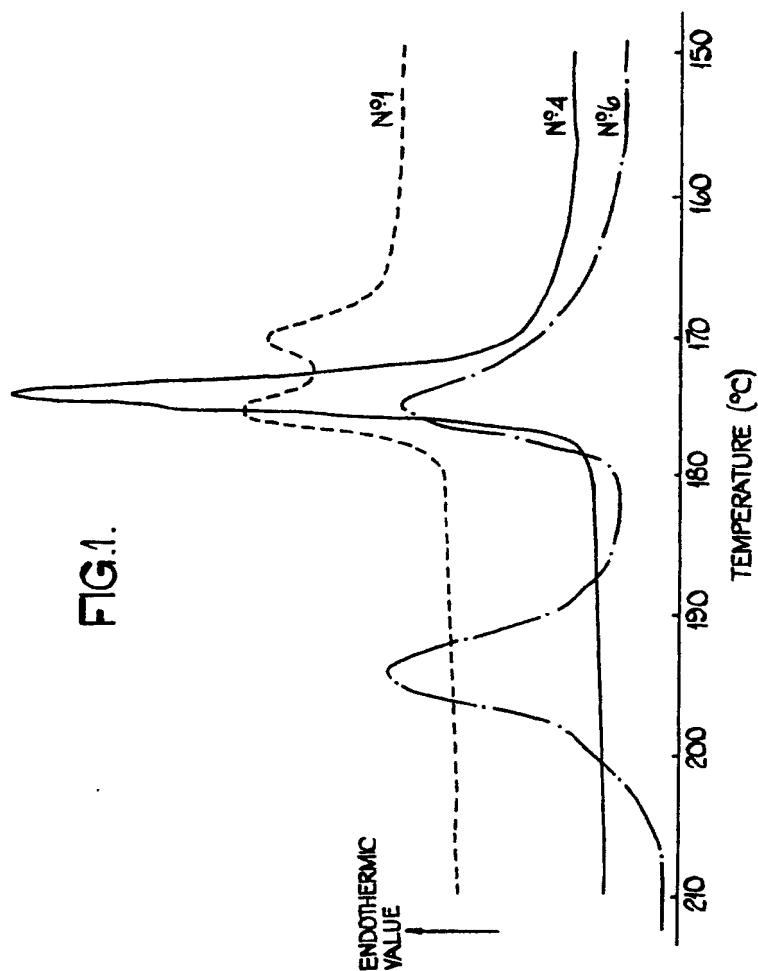
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COMPLETE SPECIFICATION

2 SHEETS

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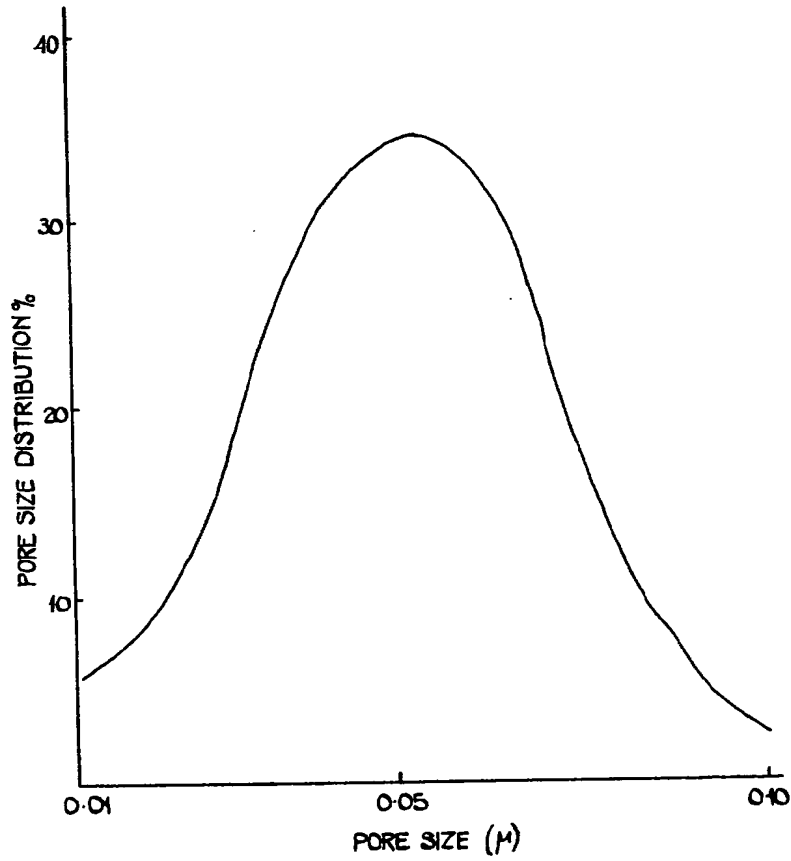
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COMPLETE SPECIFICATION

2 SHEETS

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**Sheet 2**

FIG.2.



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